

(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 690 117 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

03.01.1996 Bulletin 1996/01

(51) Int. Cl.⁶: **C09K 15/20**, **C07C 15/46**,
C07C 7/20

(21) Application number: **95303918.7**

(22) Date of filing: **07.06.1995**

(84) Designated Contracting States:
AT BE DE ES FR GB IT NL PT

(30) Priority: **30.06.1994 US 269307**
30.06.1994 US 269308
24.08.1994 US 295311

(71) Applicant: **BETZ EUROPE, INC.**
Trevose, PA 19053-6783 (US)

(72) Inventor: **Arhancet, Graciela Barbieri**
Katy, TX 77450 (US)

(74) Representative: **W.P. Thompson & Co.**
Liverpool L1 3AB (GB)

(54) Compositions and methods for inhibiting vinyl aromatic monomer polymerization

(57) Compositions and methods for inhibiting polymerization of vinyl aromatic monomers in oxygen-free processing systems are disclosed. The compositions comprise an oxime compound and a hydroxylamine compound and, alternatively, an oxime compound or a dinitrophenol, a hydroxylamine compound and a phenylenediamine compound. The methods comprise adding one of the compositions to the vinyl aromatic monomer in an amount ranging from 1 to about 10,000 parts per million parts monomer. An improved method for inhibiting the polymerization of vinyl aromatic monomers with a hydroxylamine compound is also disclosed. The improvement provides for adding a catalytic amount of a phenylenediamine compound to the vinyl aromatic monomer system while replacing any phenylenediamine compound lost as a result of physical removal from the system via the waste stream.

EP 0 690 117 A2

Description**FIELD OF THE INVENTION**

5 This invention relates to compositions and methods for inhibiting the unwanted polymerization of vinyl aromatic monomers during processing.

BACKGROUND OF THE INVENTION

10 Common industrial methods for producing styrene typically include separation and purification processes such as distillation to remove unwanted impurities. Unfortunately, purification processes carried out at elevated temperatures result in an increased rate of undesired polymerization. Distillation is generally carried out under vacuum to minimize loss of monomer. The presence of oxygen, although virtually excluded in styrene distillation, will also promote polymerization of the monomer.

15 This polymerization results not only in loss of desired monomer end-product, but also in the loss of production efficiency caused by polymer formation and/or agglomeration of polymer on process equipment. Thermal polymerization of styrene monomer results in formation of normal (i.e., linear) polymer. This resulting polystyrene polymer is characterized by its glassy and transparent appearance and its solubility in the styrene monomer and many organic solvents.

SUMMARY OF THE INVENTION

20 The present invention provides for methods for inhibiting the polymerization of vinyl aromatic monomers, such as styrene, and compositions comprising synergistic combinations of actives. The present inventor has discovered that a composition of an oxime compound and a hydroxylamine compound, as well as a composition of an oxime compound or a dinitrophenol compound with a hydroxylamine compound and a phenylenediamine compound, will effectively inhibit the unwanted polymerization of vinyl aromatic monomers during their processing.

25 The present inventor has further discovered that effective inhibition of styrene polymerization is achieved under oxygen-free conditions using a hydroxylamine compound as the polymerization inhibiting compound and a phenylenediamine compound which acts as a catalyst in accelerating the reaction between the hydroxylamine compound and free radicals present in the monomer system.

BRIEF DESCRIPTION OF THE DRAWINGS

35 Fig. 1 is a schematic diagram of one embodiment of the process of the present invention utilizing three process columns in a styrene monomer purification process.

DESCRIPTION OF THE RELATED ART

40 The compounds generally used commercially to prevent polymerization of vinyl aromatic monomers are of the dinitrophenolic type. For example, U.S. 4,105,506, Watson, et al., teaches the use of 2,6-dinitro-p-cresol as polymerization inhibitor of vinyl aromatic compounds. U.S. 4,466,905, Butler, et al., teaches that 2,6-dinitro-p-cresol and p-phenylenediamines will inhibit polymerization in the distillation column if oxygen is present. U.S. 4,774,374, Abruscato, et al., teaches compositions and processes for inhibiting the polymerization of a vinyl aromatic compound employing an oxygenated species formed by the reaction of oxygen and a N-aryl-N'-alkyl-p-phenylenediamine. U.S. 4,720,566, Martin, teaches methods and compositions for inhibiting polymerization of acrylonitrile in the quench tower, no oxygen excluded, using a hydroxylamine compound and a phenyl-p-phenylenediamine compound.

45 Czechoslovakia Patent No. 163,428 teaches a method for stabilizing styrene and divinylbenzene utilizing 2,4-dinitroorthocresol and diethylhydroxylamine. European Patent Application 0 240 297 also teaches the use of this combination to inhibit polymerization of styrene. Both these disclosures treat systems at lower temperatures and higher oxygen contents. The use of diethylhydroxylamine however is problematic in styrene purification processes as it has a boiling point (125°C to 130°C at 760 mm Hg) similar to styrene and will carry over with the styrene during purification processing.

50 A variety of inhibitor compositions have been employed in styrene and other vinyl aromatic monomers to inhibit undesirable polymerization. Amongst others, agents that have been used include sulfur, p-benzoquinone, phenylenediamines, tert-butyl pyrocatechol, phenothiazine, hydroxylamines, nitrocompounds, and hindered phenols. However, many of these compounds present disadvantages such as high toxicity, instability and explosion hazard under elevated temperature, or insufficient efficacy under processing conditions (i.e., inhibitor requires oxygen to be effective). The present inventor has discovered a novel method for inhibiting vinyl aromatic monomer polymerization that avoids these problems associated with known inhibitors.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to compositions and methods for inhibiting the polymerization of vinyl aromatic monomers in an oxygen-free vinyl aromatic monomer processing system comprising adding to the monomers a combination of an oxime compound and a hydroxylamine compound, or in an alternative embodiment, a combination of an oxime compound or a dinitrophenol compound, a hydroxylamine compound, and a phenylenediamine compound.

The compositions of the present invention prove effective at inhibiting the polymerization of vinyl aromatic monomers under monomer processing conditions. These processing conditions include but are not limited to the purification and distillation processes of vinyl aromatic monomers.

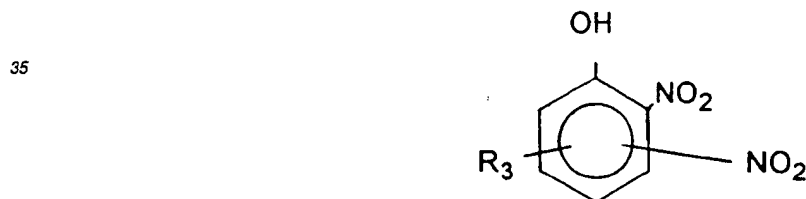
The vinyl aromatic monomers that can be treated by the present invention include but are not limited to styrene, bromostyrene, divinylbenzene and α -methylstyrene. The compositions of the present invention are particularly efficacious at inhibiting polymerization of styrene monomer. The phrase "oxygen-free processing conditions" is meant to define the substantially oxygen free conditions under which vinyl aromatic monomers, particularly styrene, are processed. These conditions, exemplified by distillation and purification processes, generally have less than 2 parts per million oxygen present and preferably less than 1 part per million oxygen per parts styrene.

The oxime compounds generally have the formula:



wherein R_1 and R_2 are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, alkylhydroxyaryl or arylhydroxyalkyl groups having three to about twenty carbon atoms. The preferred oxime compounds are salicylaldoxime, 5-dodecyl-salicylaldoxime and alkyl acetophenone oxime.

The dinitrophenol compounds generally have the structure:



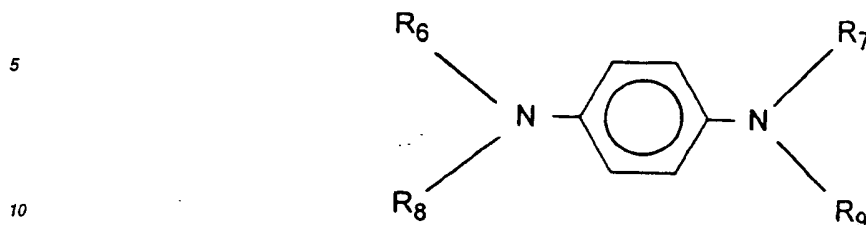
wherein R_3 is hydrogen or C_1 to C_{12} alkyl.

The hydroxylamine compounds useful in this invention generally have the formula:



wherein R_4 and R_5 are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, or hydroxyalkyl groups and preferably have three to about twenty carbon atoms. The preferred hydroxylamine compound is bis-(hydroxypropyl)hydroxylamine (HPHA).

The phenylenediamine compounds useful in this invention generally have the formula:



wherein R_6 , R_7 , R_8 and R_9 are the same or different and are hydrogen, alkyl, aryl, alkaryl or aralkyl groups having one to about twenty carbon atoms. The preferred phenylenediamine compounds are N,N'-di-sec-butyl-p-phenylenediamine and N-phenyl-N'-(1,4-dimethylpentyl)-p-phenylenediamine.

The compositions of the present invention prove effective at inhibiting the polymerization of vinyl aromatic monomers during oxygen-free processing. The inventive compositions provide enhanced activity over each separate component in styrene monomer undergoing distillation and purification processes at elevated temperatures. Styrene is typically processed at temperatures between 95 and 125°C. The compositions of the present invention prove particular efficacy in higher temperature (>110°C) styrene monomer processing systems.

The total amount of oxime compound and hydroxylamine compound (composition I), oxime compound, hydroxylamine compound and phenylenediamine compound (composition II) and dinitrophenol compound, hydroxylamine compound and phenylenediamine compound (composition III) used in the methods of the present invention is that amount which is sufficient to inhibit polymerization and will vary according to the conditions under which the vinyl aromatic monomer is being processed and exposed to high temperatures. At higher temperature and higher monomer contamination, larger amounts of polymerization inhibiting composition are generally required.

Preferably, the total amount of composition I, composition II or composition III added to the vinyl aromatic monomer ranges from 1 to about 10,000 parts per million parts monomer. More preferably, the treatment range is from about 5 parts to about 500 parts of the composition per million parts monomer.

The weight ratio of oxime compound to hydroxylamine compound in composition I ranges from about 9:1 to 1:9 with 2:1 to 9:1 preferred. The weight ratio of oxime to hydroxylamine to phenylenediamine in composition II ranges from about 1-9 to 1-9 to 1-9. The weight ratio of dinitrophenol compound to hydroxylamine compound to phenylenediamine compound ranges from 1:9:1 to 9:1:9 with a weight ratio of 1:1:1 preferred.

The compositions of the present invention can be added to the vinyl aromatic monomer by any conventional method, either as individual ingredients or as a combination of ingredients. It is preferred for both composition I, II and III that they are added as a single treatment composition.

The compositions of the present invention may be added to the vinyl aromatic monomer as either a dispersion or as a solution using suitable liquid carrier or solvent. Any solvent that is compatible with the individual ingredients of the composition and the vinyl aromatic monomer may be employed.

Accordingly, it is possible therefor to produce a more effective vinyl aromatic monomer polymerization inhibition treatment than is obtainable by the use of any one ingredient alone when measured at comparable treatment levels. This enhanced activity as evidenced by both composition I, composition II and composition III, allows for the concentration of each of these ingredients to be lowered and the total quantity of polymerization inhibitor required, particularly at higher processing temperatures, may be reduced.

The preferred inventive embodiment of composition I employs bis-(hydroxypropyl)hydroxylamine with salicylaldoxime. The preferred inventive embodiment of composition II employs bis-(hydroxypropyl)hydroxylamine, N,N'-di-sec-butyl-p-phenylenediamine with salicylaldoxime. The preferred inventive embodiment of composition III employs bis-(hydroxypropyl)hydroxylamine and N,N'-di-sec-butyl-p-phenylenediamine with 4,6-dinitro-o-cresol and 2-sec-butyl-4,6-dinitrophenol, respectively.

The present invention also further discloses methods for inhibiting the polymerization of vinyl aromatic monomers in an oxygen-free vinyl aromatic processing system containing a continuous feed stream of vinyl aromatic monomer, a continuous recycle stream returning to said feed stream, at least one process column, and a waste stream, the improvement comprising the steps of:

- a) adding to said feed stream a sufficient polymerization inhibiting amount of a hydroxylamine compound;
- b) adding as a catalyst a separate feed of a phenylenediamine compound to said feed stream in an amount sufficient to ensure that said phenylenediamine is present in said process column in a 1:9 to 9:1 weight ratio with said hydroxylamine compound;

c) replacing the amount of phenylenediamine compound physically removed from said system through said waste stream by adding an amount sufficient to compensate for the amount of said phenylenediamine compound removed and to maintain a constant level of said phenylenediamine compound in a 1:9 to 9:1 weight ratio with said hydroxylamine compound in said system.

5

The accompanying drawing is a simplified schematic flow sheet exemplifying the purification of vinyl aromatic monomer (styrene) in a low temperature vacuum distillation unit. A feed consisting mainly of ethylbenzene and styrene is fed through line 10 into a benzene/toluene fractionation column 11 where benzene and toluene are removed from a top line 13 to storage. The bottoms consisting mostly of ethylbenzene and styrene is fed through line 12 to an EB (ethylbenzene) recycle column 14. Ethylbenzene is removed through line 16 for return to the styrene synthesis facility. The EB

recycle column bottoms consisting of styrene and high boiling impurities is fed through line 15 to a finishing column 17. Finished styrene is removed to storage through line 19 and styrene, polymer and high boiling point compounds are passed through line 18 to a tar recovery system, 20 and 25. Tar bottoms from 20 are split through line 21, a continuous recycling stream which recycles to the feed line 10 and through line 23 to a tar recover column 25. Tar waste exits the

tar recovery column 25 through waste stream 24 and finished styrene flows through line 26 for storage. In the process of the instant invention, the polymerization inhibiting compound, hydroxylamine compound, and the catalytic agent, phenylenediamine compound are added separately to the feed stream. The hydroxylamine compound can be added continuously or intermittently depending upon its consumption at inhibiting polymerization but is added to maintain an amount necessary to inhibit polymerization while the phenylenediamine is fed to the system, after the initial addition, to compensate for that amount of phenylenediamine physically removed via the waste stream. This ensures that the phenylenediamine, which is not consumed through inhibitory action, is maintained in the system in an amount necessary to act as a catalyst improving the inhibitory action of the hydroxylamine compound.

The hydroxylamine compound may be inputted at any point of the purification process to adjust for unexpected consumption. Thus, the hydroxylamine compound may be added at any time during the styrene monomer processing but it is preferably continuously added at the front of the processing system with the crude styrene in an amount necessary to inhibit styrene polymerization during the purification process.

The amount of phenylenediamine compound which is added is that sufficient to ensure its presence in the columns present in the purification apparatus. This amount is readily determined by sampling the columns' bottoms and analyzing by gas chromatography or a spectrophotometric analytical technique. The feed amount can then be used with the amount returned via the continuous recycle stream to determine the amounts of replacement phenylenediamine added to act as catalyst in further processing.

The amount of phenylenediamine compound removed with the waste stream is readily determined by sampling of the waste stream. A sufficient amount of phenylenediamine compound can then be fed through the feed stream to ensure that catalytic activity continues to occur in the processing system.

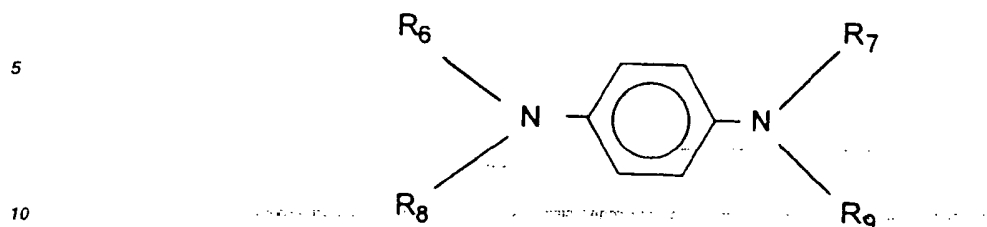
The present inventor has discovered that in the presence of a catalyst, phenylenediamine compound, polymerization is inhibited throughout the purification system. The hydroxylamine compound is more effective at inhibiting polymerization because the phenylenediamine compound improves the inhibiting action of the hydroxylamine compound more than in absence of any phenylenediamine compound. This results in a more efficient and less costly means for inhibiting the unwanted polymerization of styrene monomer and a lower amount of addition of hydroxylamine to supplement that used to inhibit polymerization.

The hydroxylamine compounds useful in this aspect of the invention generally have the formula:



wherein R_4 and R_5 are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, or hydroxyalkyl groups and preferably have three to about twenty carbon atoms. The preferred hydroxylamine compound is bis-(hydroxypropyl)hydroxylamine (HPHA).

The phenylenediamine compounds useful as catalysts in this invention generally have the formula:



15 wherein R_6 , R_7 , R_8 and R_9 are the same or different and are hydrogen, alkyl, aryl, alkaryl or aralkyl groups having one to about twenty carbon atoms. The preferred phenylenediamine compound is N,N'-di-sec-butyl-p-phenylenediamine.

The term "catalytic" referring to the phenylenediamine compound defines that the phenylenediamine compound, under the oxygen-free conditions of hydroxylamine compound inhibiting styrene polymerization, improves the inhibiting effect of hydroxylamine while remaining unconsumed by the process. This catalytic effect results in the slower consumption of hydroxylamine compound while the concentration and amount of phenylenediamine compound remains the same.

20 As indicated, the styrene monomer and processing environment must be oxygen-free for the catalytic effects of the phenylenediamine compound to be realized. When oxygen is present, both the hydroxylamine compound and phenylenediamine compound will be consumed, albeit the phenylenediamine compound at a slower rate.

The amount of hydroxylamine compound utilized in the methods of the present invention is that amount which is necessary to inhibit polymerization of the styrene. This amount will vary according to the conditions under which the styrene is being processed, the amount of unreacted starting materials and distillable byproducts, and the temperature of the system.

25 Preferably, the total amount of hydroxylamine compound added to the styrene feed is from about 10 parts to about 10,000 parts per million parts styrene by weight. More preferably, the amount of hydroxylamine compound ranges from about 10 parts to about 2000 parts per million parts by weight styrene. The weight ratio of phenylenediamine added to this hydroxylamine compound added ranges from 1:9 to 9:1 and is preferably about 1:1 to about 1:2.

30 The hydroxylamine compound can be added to the styrene monomer by any conventional method. The hydroxylamine may be added as either a dispersion or as a solution using a suitable liquid carrier or solvent. Any solvent that is compatible with both the styrene monomer and phenylenediamine compound may be employed.

35 This invention will now be further described with reference to a number of specific examples which are to be regarded solely as illustrative and not as restricting the scope of the invention.

Examples

40 In order to evaluate the improved polymerization inhibition of the inventive compositions and to demonstrate the enhanced activity of each composition, styrene polymerization testing was performed.

Uninhibited styrene (5 mL) was placed in a test tube and the appropriate amount of treatment was added. The tube was capped with a septum and argon was bubbled through the liquid at 15 mL/min for 3 minutes. Then, the tubes were placed in an oil bath heated to 120°C for 2 hours. The amount of polystyrene formed was determined by methanol precipitation. Results of this testing are summarized in Table I.

TABLE I

Styrene Polymerization Test
Uninhibited Styrene
120°C

| <u>Treatment</u> | <u>Dose (ppm)</u> | <u>Percent Polymer</u> |
|------------------|-------------------|------------------------|
| SA | 600 | 19.40 |
| DDSA | 600 | 19.40 |
| AAO | 600 | 18.68 |
| HPHA | 600 | 8.56 |
| HPHA/SA | 300/300 | 0.93 |
| HPHA/SA | 150/450 | 7.27 |
| HPHA/SA | 450/150 | 0.67 |
| HPHA/SA | 200/400 | 4.40 |
| HPHA/SA | 400/200 | 0.89 |
| HPHA/SA | 100/500 | 10.22 |
| HPHA/SA | 500/100 | 1.44 |
| HPHA/DDSA | 300/300 | 1.60 |
| HPHA/DDSA | 450/150 | 0.70 |
| HPHA/AAO | 300/300 | 4.84 |
| HPHA/AAO | 450/150 | 5.01 |

SA is salicylaldoxime

DDSA is 5-dodecylsalicylaldoxime, available from Henkel as Aloxime 800

AAO is alkyl acetophenone oxime, available from Henkel as Aloxime 840

HPHA is bis-(hydroxypropyl)hydroxylamine

The results of this testing indicate that composition I, oxime compound and hydroxylamine compound, provides enhanced activity over that of either ingredient alone at inhibiting the polymerization of styrene. Hydroxylamine compounds are known polymerization inhibitors for styrene, yet the polymerization inhibition of the combination exceeded that of a hydroxylamine compound employed alone.

Further testing was performed utilizing the procedure described for Table I for composition II. These results are reported in Table II.

TABLE II

Styrene Polymerization Test
Uninhibited Styrene
120°C

| <u>Treatment</u> | <u>Dose (ppm)</u> | <u>Percent Polymer</u> |
|------------------|-------------------|------------------------|
| PD/HPHA | 200/300 | 4.10 |
| SA | 600 | 19.40 |
| DDSA | 600 | 19.40 |
| AAO | 600 | 18.68 |
| PDA/HPHA/SA | 200/300/100 | 0.24 |
| PDA/HPHA/SA | 200/300/50 | 0.51 |
| PDA/HPHA/SA | 200/300/25 | 1.30 |
| PDA/HPHA/DDSA | 200/300/100 | 0.92 |
| PDA/HPHA/AAO | 200/300/100 | 1.76 |

PDA is N,N'-di-sec-butyl-p-phenylenediamine

HPHA is bis-(hydroxypropyl)hydroxylamine

SA is salicylaldoxime

DDSA is 5-dodecylsalicylaldoxime, available from Henkel as Aloxime 800.

AAO is alkyl acetophenone oxime, available from Henkel as Aloxime 840.

The results of this testing indicate that composition II of the present invention, oxime compound, hydroxylamine compound and phenylenediamine compound, provides enhanced activity over that of hydroxylamine/phenylenediamine combination or the use of oxime compounds singly as polymerization inhibitors. These results, as in Table I, show that the inventive compositions provide enhanced activity at inhibiting polymerization over that of the individual components at elevated styrene processing temperatures. Further, the addition of an oxime compound to a known polymerization inhibitor, hydroxylamine compound and phenylenediamine, resulted in better inhibition of polymerization than the known inhibitor pair.

TABLE III

Styrene Polymerization Test
Uninhibited Styrene
120°C

| <u>Treatment</u> | <u>Dose (ppm)</u> | <u>Percent Polymer</u> |
|------------------|-------------------|------------------------|
| Blank | ----- | 23.3 |
| DNOC | 300 | 2.15 |
| DNBP | 300 | 1.77 |
| PDA | 300 | 21.06 |
| HPHA | 300 | 17.96 |
| PDA:HPHA:DNOC | 100:100:100 | 1.38 |
| PDA:HPHA:DNOC | 75:150:75 | 1.78 |
| PDA:HPHA:DNOC | 50:150:100 | 1.23 |
| PDA:HPHA:DNBP | 100:100:100 | 1.02 |
| PDA:HPHA:DNBP | 50:150:100 | 0.79 |

DNOC is 4,6-dinitro-o-cresol

DNBP is 2-sec-butyl-4,6-dinitrophenol

PDA is N,N'-di-sec-butyl-p-phenylenediamine

HPHA is bis-(hydroxypropyl)hydroxylamine

These test results demonstrate the enhanced polymerization inhibition of the three component combination of DNOC/DNBP, HA and PDA. Unexpected results were evidenced in a range from 1:1:1 to 1:3:2 at inhibiting styrene polymerization at higher (120°C) styrene processing temperatures.

Uninhibited styrene (100 mL) was placed in a 250-mL three-necked flask fitted with a bubbler, a septa, and a condenser. The appropriate treatment was added and argon was bubbled through the solution at 10 mL/min for 10 minutes. Then, while argon sparging continued, the flask was immersed in an oil bath heated at 120°C. Samples (5.0 mL) were taken every 30 minutes and the amount of polymer formed was determined by methanol precipitation. The results of this testing for compositions I and II are presented below in Tables IV and V.

TABLE IV

Styrene Polymerization Test under argon
120°C

Treatment: bis-hydroxypropylhydroxylamine/salicylaldoxime
300 ppm of each

| <u>Time (min)</u> | <u>% Polymer</u> |
|-------------------|------------------|
| 30 | 0.04 |
| 60 | 0.10 |
| 90 | 0.19 |
| 120 | 0.29 |
| 150 | 0.54 |
| 180 | 3.30 |

TABLE V

Styrene Polymerization Test under argon

120°C

600 ppm total treatments, 1:2:1 ratios

| Treatment SA/HPHA/I-3 | | Treatment SA/HPHA/PDA | |
|--------------------------|-----------|--------------------------|-----------|
| Time (min) | % Polymer | Time (min) | % Polymer |
| 30 | 0.01 | 30 | 0.01 |
| 60 | 0.03 | 60 | 0.02 |
| 90 | 0.05 | 90 | 0.05 |
| 120 | 0.10 | 120 | 0.10 |
| 150 | 0.35 | 150 | 0.17 |
| 180 | 0.76 | 180 | 0.28 |

SA is salicylaldoxime

HPHA is bis-(hydroxypropyl)hydroxylamine

I-3 is N-phenyl-N'-(1,4-dimethylpentyl)-p-phenylenediamine

PDA is N,N'-di-sec-butyl-p-phenylenediamine

These results indicate that the inventive compositions, I and II, provide enhanced activity at inhibiting styrene polymerization at elevated process conditions and in oxygen-free processing environments. Similar testing was performed for Composition III. Table VI reports the efficacy of this composition at inhibiting styrene polymerization.

TABLE VI

Styrene Polymerization Test

Uninhibited Styrene

120°C

Treatment: PDA/HPHA/DNBP in a 200:200:100 ppm ratio

| Time (hrs.) | % Polymer |
|-------------|-----------|
| 1 | 0.07 |
| 2 | 0.31 |
| 3 | 0.49 |
| 4 | 1.10 |

PDA is N,N'-di-sec-butyl-p-phenylenediamine

HPHA is bis-(hydroxypropyl)hydroxylamine

DNBP is 2-sec-butyl-4,6-dinitrophenol

70 ml of freshly distilled uninhibited styrene was placed in a three-necked flask fitted with a condenser, a bubbler, and a rubber septum. The appropriate amount of phenylenediamine compound and hydroxylamine compound was added and argon was bubbled through the liquid at 15 ml/min with stirring from a magnetic stirrer. After 20 minutes the flask was immersed in a heated oil-bath. Argon bubbling continued through the test as samples were taken every 30 minutes. The amount of polystyrene formed was determined by methanol precipitation. Phenylenediamine concentration was determined by capillary gas chromatography using an internal standard. Hydroxylamine concentration was measured by HPLC with an electrochemical detector. The results of this testing are presented in Tables VII and VIII.

TABLE VII

Styrene (pure) under argon test at 120°C

Treatment: 30 ppm hydroxypropylhydroxylamine (HPHA)

30 ppm N,N'-di-sec-butyl-p-phenylenediamine (PDA)

| Time (min) | Polymer Formed (mg/5 ml) | PDA Remaining (ppm) |
|---------------|-----------------------------|------------------------|
| 0 | 0 | 30 |
| 15 | 3 | 29 |
| 30 | 60 | 30 |
| 45 | 126 | 30 |
| 60 | 218 | 30 |

TABLE VIII

Styrene (pure) under argon test at 120°C

Treatment: 75 ppm HPHA and 75 ppm PDA

| Time (min) | PDA (ppm) | HPHA (ppm) | Polymer Formed (mg/5 ml) |
|---------------|--------------|---------------|-----------------------------|
| 0 | 75 | 75 | 0 |
| 45 | 75 | 78 | 0 |
| 90 | 75 | 74 | 0 |
| 135 | 75 | 62 | 0 |
| 180 | 75 | 47 | 64 |
| 225 | 75 | 56* | 224 |
| 270 | 75 | 41* | 648 |

*possible response variation in the detector.

This testing shows that polymerization is being inhibited while the amount of the catalyst, PDA, remains constant. This indicates that the PDA acts to activate or catalyze the reaction involved in inhibiting polymerization.

An experiment was utilized to demonstrate the effect of HPHA concentration of the onset of polymerization. The reflux under argon of Table VIII was repeated at 120°C on pure styrene treated with 75 ppm of HPHA and 75 ppm of PDA. After 135 minutes of heating, the polymerization induction time under those conditions, an additional 35 ppm of HPHA was added. These results are shown in Table IX.

TABLE IX

| Time (min) | Polymer Formed (mg/5 ml) | PDA Remaining (ppm) | HPHA Remaining (ppm) |
|------------|--------------------------|---------------------|----------------------|
| 0 | 0 | 75 | 75 |
| 45 | 0 | 74 | 78 |
| 90 | 0 | 75 | 74 |
| 135 | 0 | 75 | 62 |
| 180 | 0 | 75 | 47 |
| 225 | 0 | 75 | 48 |
| 270 | 0 | 75 | 41 |

*35 ppm of HPHA were added.

These results demonstrate that styrene polymerization is inhibited by HPHA while PDA is not consumed in the reactions. Satisfactory inhibition was achieved over an extended time period after the induction period by replenishing the supply of the inhibitor, HPHA, as needed.

Another polymerization test was run with no argon purging and only PDA added to the styrene results are shown in Table X.

TABLE X

Styrene (pure) without argon purging at 120°C

Treatment: 100 ppm PDA

| Time (min) | Polymer Formed (mg/5 ml) | PDA Remaining (ppm) |
|---------------|-----------------------------|------------------------|
| 0 | 0 | 100 |
| 30 | 2 | 110 |
| 60 | 3 | 47 |
| 135 | 73 | not detected |
| 150 | 96 | not detected |

This testing shows that in the presence of oxygen, the phenylenediamine will inhibit polymerization but within one hour will totally be depleted. This demonstrates that when a known inhibitor, PDA, is employed alone in the presence of oxygen, it will inhibit polymerization until it is consumed. However, the same inhibitor when employed with HPHA in an oxygen-free system will catalyze and make more efficient the polymerization inhibition.

While this invention has been described with particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

Claims

1. A vinyl aromatic monomer polymerization inhibiting composition comprising an oxime compound and a hydroxylamine compound.

2. A composition as claimed in claim 1, wherein said oxime compound has the formula.



10 wherein R_1 and R_2 are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, alkylhydroxyaryl or arylhydroxyalkyl groups and have three to about twenty carbon atoms.

3. A composition as claimed in claim 1, wherein said oxime compound is selected from the group consisting of salicylaldoxime, 5-dodecylsalicylaldoxime and alkyl acetophenone oxime.

- 15 4. A composition as claimed in claim 1, wherein said hydroxylamine compound has the formula



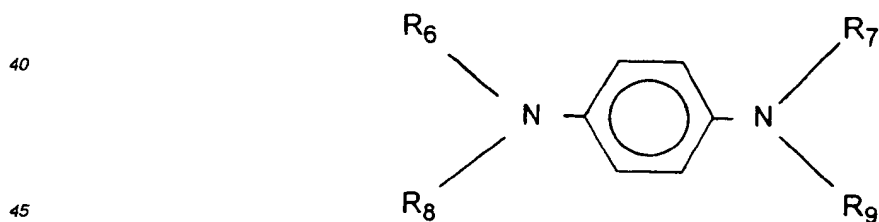
25 wherein R_4 and R_5 are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, or hydroxyalkyl groups and have three to about twenty carbon atoms.

5. A composition as claimed in any one of the preceding claims, wherein said hydroxylamine compound is bis-(hydroxypropyl) hydroxylamine.

- 30 6. A composition as claimed in any one of the preceding claims, wherein said oxime compound and said hydroxylamine compound are in a weight ratio from about 9:1 to 1:9.

7. A composition as claimed in any one of the preceding claims, further comprising a phenylenediamine compound.

- 35 8. A composition as claimed in claim 7, wherein said phenylenediamine compound has the formula:



50 wherein R_6 , R_7 , R_8 and R_9 are the same or different and are hydrogen, alkyl, aryl, alkaryl or aralkyl groups having one to about twenty carbon atoms.

9. A composition as claimed in claim 7 or 8, wherein said phenylenediamine compound is selected from the group consisting of N,N'-di-sec-butyl-p-phenylenediamine and N-phenyl-N'-(1,4-dimethylpentyl)-p-phenylenediamine.

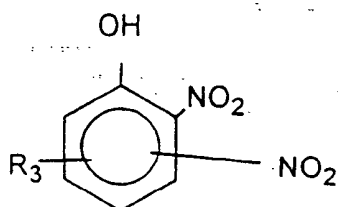
- 55 10. A composition as claimed in claim 7, 8 or 9, wherein the weight ratio of oxime compound to hydroxylamine compound to phenylenediamine compound is about 1-9 to 1-9 to 1-9.

11. A method for inhibiting the polymerization of vinyl aromatic monomers in an oxygen-free vinyl aromatic monomer processing system comprising adding an effective polymerization inhibiting amount of a composition as claimed in any one of the preceding claims.

12. A method as claimed in claim 11, wherein said composition is added to said monomer in an amount ranging from 1 part to about 10,000 parts per million parts monomer.

13. A method for inhibiting the polymerization of vinyl aromatic monomers in an oxygen-free vinyl aromatic monomer processing system comprising adding an effective polymerization inhibiting amount of a dinitrophenol compound, a hydroxylamine compound, and a phenylenediamine compound.

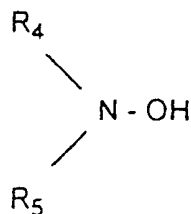
14. A method as claimed in claim 13, wherein said dinitrophenol compound has the formula:



wherein R_3 is hydrogen or C_1 to C_{12} alkyl.

15. A method as claimed in claim 13, wherein said dinitrophenol compound is selected from the group consisting of 4,6-dinitro-o-cresol, 2,6-dinitro-p-cresol and 2-sec-butyl-4,6-dinitrophenol.

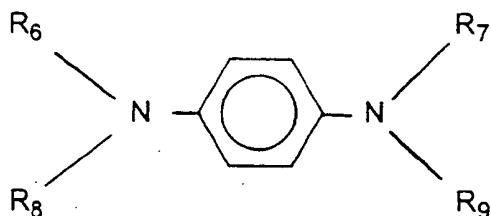
16. A method as claimed in claim 13, 14 or 15, wherein said hydroxylamine compound has the formula:



wherein R_4 and R_5 are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, or hydroxyalkyl groups and preferably have about three to about twenty carbon atoms, except when R_2 is H, then R_3 is C_6 alkyl to C_{20} alkyl.

17. A method as claimed in claim 13, 14 or 15, wherein said hydroxylamine compound is bis-hydroxypropylhydroxylamine.

18. A method as claimed in any one of claims 13 to 17, wherein said phenylenediamine compound has the formula:



wherein R_6 , R_7 , R_8 and R_9 are the same or different and are hydrogen, alkyl, aryl, alkaryl or aralkyl groups having one to about twenty carbon atoms.

19. A method as claimed in any one of claims 13 to 18, wherein said phenylenediamine compound is N,N'-di-sec-butyl-p-phenylenediamine.

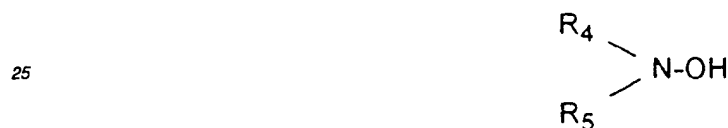
20. A method as claimed in any one of claims 13 to 19, wherein said dinitrophenol compound, hydroxylamine compound and phenylenediamine compound are added to said vinyl aromatic monomer in an amount ranging from 1 to about 10,000 parts per million parts monomer.

5 21. The method as claimed in any one of claims 13 to 20, wherein said vinyl aromatic monomer has a temperature of 110°C or higher.

22. A method for inhibiting the polymerization of vinyl aromatic monomers in an oxygen-free vinyl aromatic processing system containing a continuous feed stream of vinyl aromatic monomer, a continuous recycle stream returning to said feed stream, at least one process column, and a waste stream, comprising the steps of:

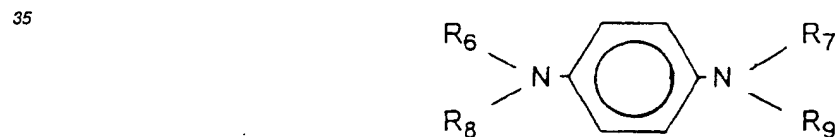
- 10
- a) adding to said feed stream a sufficient polymerization inhibiting amount of a hydroxylamine compound;
 - b) adding as a catalyst a separate feed of a phenylenediamine compound to said feed stream in an amount sufficient to ensure that said phenylenediamine is present in said process column in a 1:9 to 9:1 weight ratio with said hydroxylamine compound;
 - 15 c) replacing the amount of phenylenediamine compound physically removed from said system through said waste stream by adding an amount sufficient to compensate for the amount of said phenylenediamine compound removed and to maintain a constant level of said phenylenediamine compound in a 1:9 to 9:1 weight ratio with said hydroxylamine compound in said system.

20 23. A method as claimed in claim 22 wherein said hydroxylamine compound has the formula



30 wherein R_4 and R_5 are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, or hydroxyalkyl groups, and have one to about twenty carbon atoms.

24. A method as claimed in claim 22 or 23, wherein said phenylenediamine compound has the formula



wherein R_6 , R_7 , R_8 and R_9 are the same or different and are hydrogen, alkyl, aryl, alkaryl or aralkyl groups having one to about twenty carbon atoms.

45 25. A method as claimed in any one of claims 22 to 24, wherein said phenylenediamine compound is N,N'-di-sec-butyl-p-phenylenediamine.

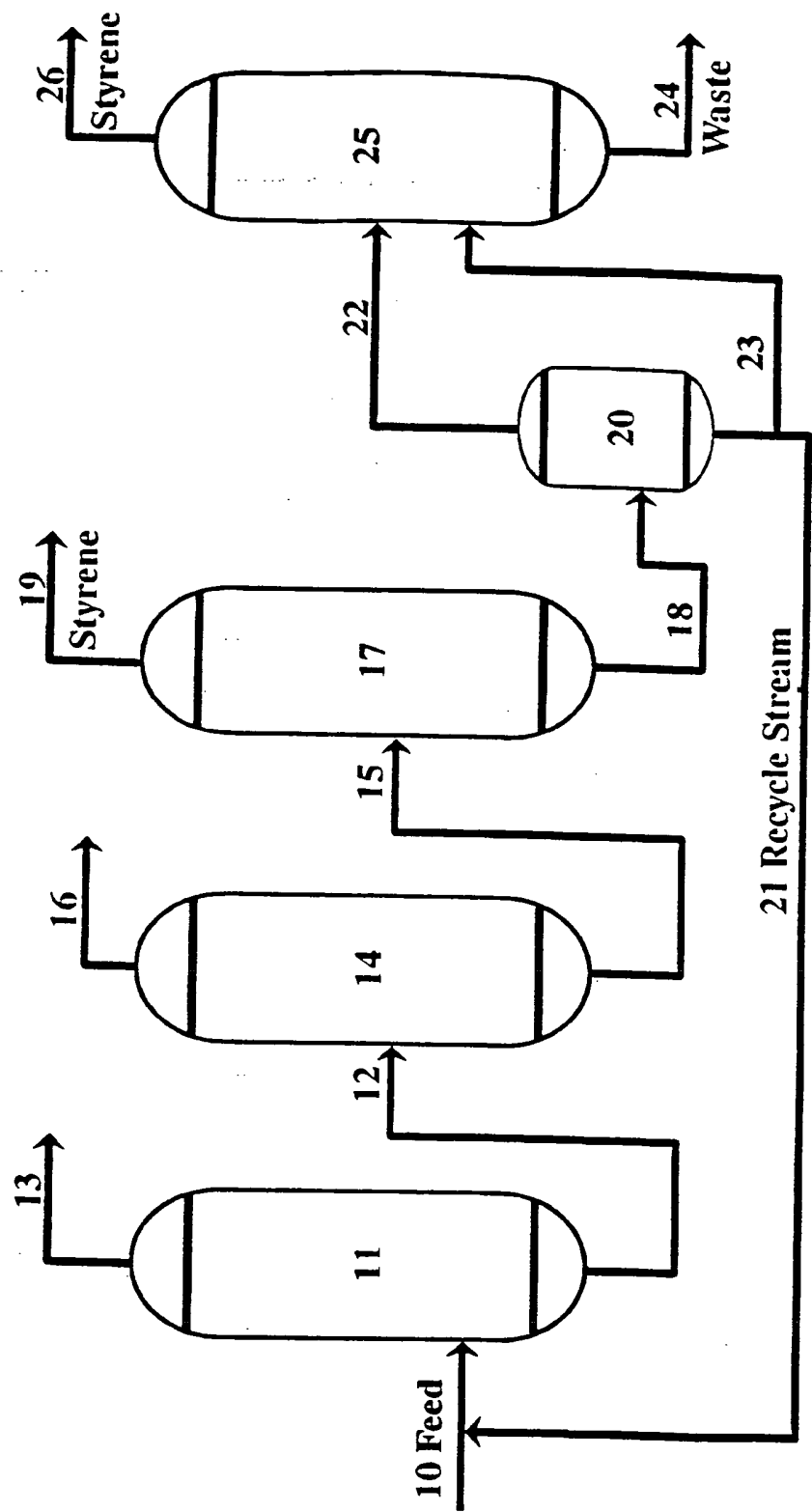
26. A method as claimed in any one of claims 22 to 25, wherein said hydroxylamine compound is added to said system in an amount ranging from 20 parts to about 10,000 parts per million parts vinyl monomer in said system.

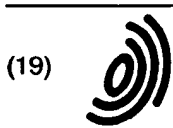
50 27. A method as claimed in any one of claims 22 to 26, wherein the weight ratio of phenylenediamine compound to hydroxylamine compound ranging from 1:1 to 2:1.

28. A method as claimed in any one of claims 11 to 27, wherein said vinyl aromatic monomer is styrene.

55 29. A method as claimed in any one of claims 22 to 28, wherein said system contains three process columns.

Styrene Purification





Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 690 117 A3**

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:
07.02.1996 Bulletin 1996/06

(51) Int. Cl.⁶: **C09K 15/20**, **C07C 15/46**,
C07C 7/20

(43) Date of publication A2:
03.01.1996 Bulletin 1996/01

(21) Application number: **95303918.7**

(22) Date of filing: **07.06.1995**

(84) Designated Contracting States:
AT BE DE ES FR GB IT NL PT

(30) Priority: **30.06.1994 US 269307**
30.06.1994 US 269308
24.08.1994 US 295311

(71) Applicant: **BETZ EUROPE, INC.**
Trevose, PA 19053-6783 (US)

(72) Inventor: **Arhancet, Graciela Barbieri**
Katy, TX 77450 (US)

(74) Representative: **W.P. Thompson & Co.**
Liverpool L1 3AB (GB)

(54) **Compositions and methods for inhibiting vinyl aromatic monomer polymerization**

(57) Compositions and methods for inhibiting polymerization of vinyl aromatic monomers in oxygen-free processing systems are disclosed. The compositions comprise an oxime compound and a hydroxylamine compound and, alternatively, an oxime compound or a dinitrophenol, a hydroxylamine compound and a phenylenediamine compound. The methods comprise adding one of the compositions to the vinyl aromatic monomer in an amount ranging from 1 to about 10,000 parts per million parts monomer. An improved method for inhibiting the polymerization of vinyl aromatic monomers with a hydroxylamine compound is also disclosed. The improvement provides for adding a catalytic amount of a phenylenediamine compound to the vinyl aromatic monomer system while replacing any phenylenediamine compound lost as a result of physical removal from the system via the waste stream.

EP 0 690 117 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 3918

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|---|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| A | EP-A-0 594 341 (BETZ EUROPE) --- | | C09K15/20 |
| A | US-A-4 237 326 (FUGA ET AL) --- | | C07C15/46 |
| A | DE-B-11 54 455 (BADISCHE ANILIN- UND SODA-FABRIK) --- | | C07C7/20 |
| A | EP-A-0 240 297 (BETZ EUROPE) ----- | | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |
| | | | C07C C07B C09K |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 11 December 1995 | Examiner Van Geyt, J |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons</p> <p>..... & : member of the same patent family, corresponding document</p> | | | |

EPO FORM 1503 03.92 (P04C01)



European Patent
Office

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions.

namely:

See sheet -B-

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



European Patent
Office

EP 95 30 3918 -B-

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims 1-12,28 (in part):

An inhibiting composition comprising an oxime, and a hydroxylamine; its use

2. Claims 13-21,28 (in part):

A method for inhibiting polymerisation using a composition comprising a dinitrophenol, a hydroxylamine and a phenylenediamine

3. Claims 22-27,28 (in part),29:

A method for inhibiting polymerisation using a composition comprising a hydroxylamine and a phenylene-diamine

The essential technical feature of claim 1 is the presence of an oxime and a hydroxylamine: although compositions comprising a hydroxylamine are used in the methods of claims 13 and 22, the oxime is not present. In claim 13 a composition comprising a dinitrophenol is used, this compound is not present in the compositions of claims 1 and 22. As the essential technical features of each method are different, a single inventive concept is missing and no unity can be seen between the different methods.